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SYNTHESIS OF GLASS IN THE SYSTEM QUARTZ – KAOLIN – DOLOMITE

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Studies in the system kaolin – quartz – dolomite have made it possible to obtain alkali-free glasses, which are distinguished by low CLTE and higher heat resistance, and have a high softening temperature and chemical resistance to water and alkali solutions. Electron microscopy shows that the synthesized glasses possess liquation structure.

Key words: kaolin – quartz – dolomite system, alkali-free glass, liquation structure, heat resistance, chemical resistance.

It is of practical and theoretical interest to obtain alkali-free glasses and sitals based on them. The objective of our work is to synthesize glasses and sitals in the pseudoternary system quartz – kaolin – dolomite, whose components are raw materials widely occurring in nature.

To this end the phase diagram of the system quartz – kaolin – dolomite (Fig. 1) was studied. The data for constructing the phase diagram were obtained by the methods of quenching in an MHO-2 (Zeiss, Germany) heating microscope.

The investigations showed that a quite extensive zone of transparent glasses is present in the quartz – kaolin – dolomite system (Fig. 2).

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The glasses were synthesized under laboratory conditions using local raw materials, such as kaolin from the Angren deposit, vein quartz from the "Zargar" deposit, and dolomite from the Guzar deposit. The glasses were made in an electric resistance furnace with Silit rods in corundum crucibles with capacity 100 – 300 g and temperature rise rate 300 K/h.

The glassmaking temperature was 1450 °C. Homogenization and fining of the melt were observed with 1-h soaking at the maximum temperature. The melt obtained was poured onto a heated slab. Quenching was performed in air.

The structure of the glasses was studied by means of electron microscopy, which showed the presence of liquation

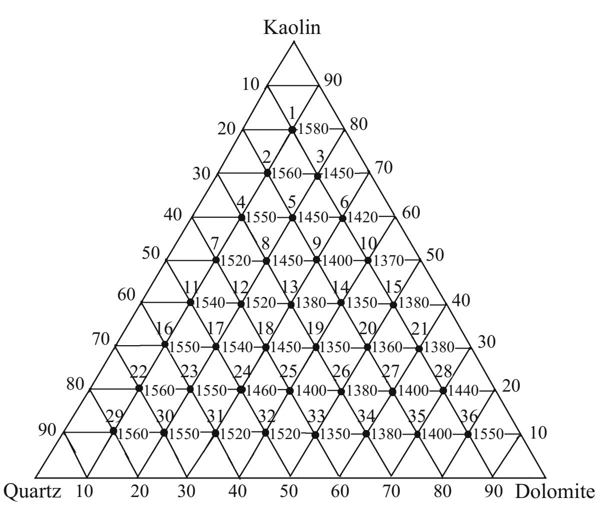

Fig. 1. Phase diagram of the quartz – kaolin – dolomite system: 1 – 36) glass numbers; glass melting temperature shown in °C.

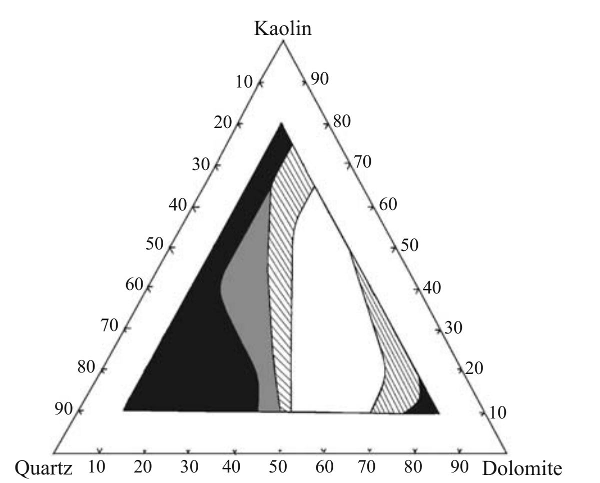

Fig. 2. Region of glass formation in the quartz – kaolin – dolomite system: ——) boundary of experimental compositions; ☐) region of transparent glasses; ▨) region of opalescent glasses; ▩) region of opacified glasses; ■) region of incomplete melting.

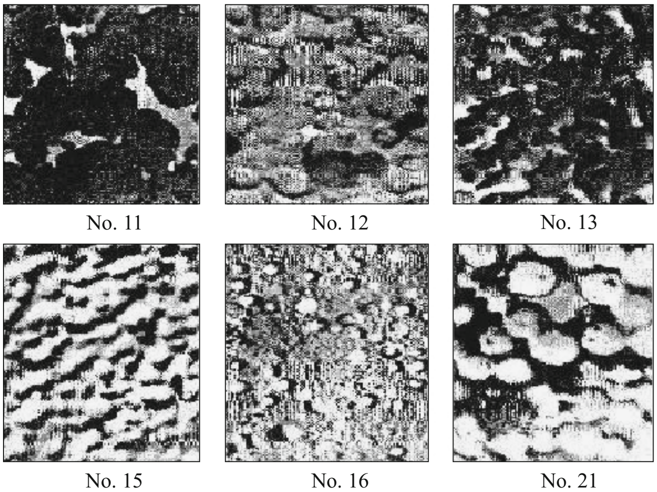

Fig. 3. Electron-microscopic photographs of glasses (× 6000). The numbers on the glasses correspond to the numbers presented in Fig. 1.

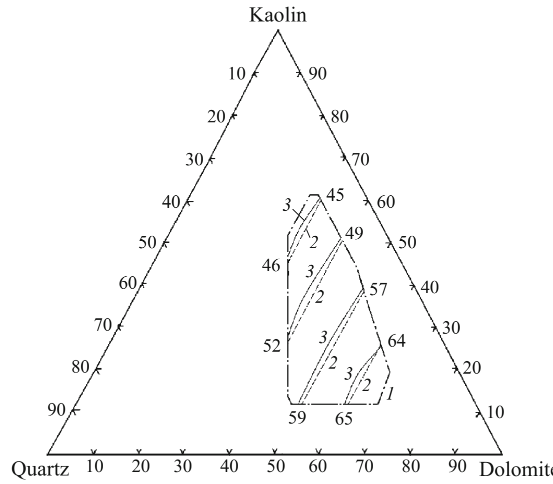

Fig. 4. CLTE of the synthesized glasses: *1*) boundary of the experimental glasses; *2*, *3*) theoretical and experimental CLTE of the glasses, respectively.

phenomena. Liquation structure is clearly recorded in the electron-microscopic photographs. This structure was acquired during cooling in opalescent and opacified glasses. XPA data confirm the liquation nature of the opacification — all experimental glasses are x-ray amorphous. Liquation is of a drop nature; framework structure is observed less often (Fig. 3).

The number of drops per unit volume and their sizes depend on the composition of the glass. The largest drops are characteristic for glasses Nos. 15, 17, 19, and 21, which contain 15 – 21%[2] CaO and 9 – 13% MgO. It was determined that adding CaO and MgO at the same time, i.e., increasing the dolomite content, has a positive effect on the quality of the liquating coatings. Intensive development of liquation was observed in the experimental compositions; this is explained by the closeness of the radii of Ca^{2+} and Mg^{2+}.

As the Al_2O_3 content (3 – 18%) in the glasses Nos. 1 – 10 increases, its homogenizing role becomes evident; there are virtually no indications of phase separation at the glass-formation stages. However, opalescence and opacification are observed in the glasses Nos. 11 – 13 when the Al_2O_3 content is increased to 18 – 22% and the SiO_2 amount is decreased to 35 – 48%. This can be explained by a decrease of the solubility of the melt. Liquation of the framework type is characteristic for these glasses.

Therefore, calcium and magnesium oxides enlarge and aluminum oxide decreases the region of liquation with the latter compound forming with calcium and magnesium silicates a relatively narrow liquation region.

The results of the investigations of the crystallization capacity of the synthesized glasses by mass crystallization are presented in Table 1.

Certain physical – chemical properties of the synthesized glasses were investigated. The differences between the computed and experimental data on the CLTE are small — 1 – 1.5%; this attests that the properties of the glasses conform to the additivity rule. The isolines of identical values of the CLTE of the glasses are presented in Fig. 4.

The softening onset temperature is one of the most important strength characteristics of glass structure. This temperature of the experimental glasses varies from 800 to 950°C (Fig. 5), and its dependence on the Al_2O_3 content is linear. This shows that there is no restructuring with increasing content of these components. The aluminum ion in the aluminate groupings enters into the general aluminate framework of the glass, promoting polymerization of the structural groupings. As a result, the structure of the glass becomes more symmetric and the amplitude of the thermal oscillations of the ions decreases. For this reason increasing the

TABLE 1.

Glass No.	Degree of crystallization at temperature,* °C					
	700	800	900	1000	1100	1200
6						
9						
10						
14						
19						
20						–
26						–
27						–
33						–
34						–

* Soaking time 1 h.

) transparent glass;) opalescence;) surface crystallization;) internal crystallization;) volume crystallization;) complete crystallization.

[2] Here and below — content by weight.

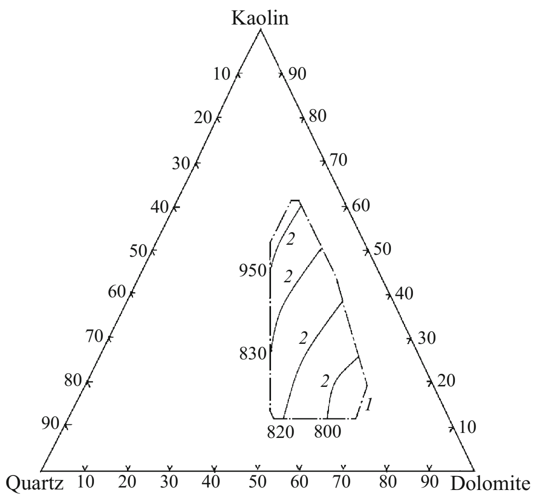

Fig. 5. Softening temperature of the synthesized glasses: *1*) boundary of the experimental glasses; *2*) softening temperature of the glasses.

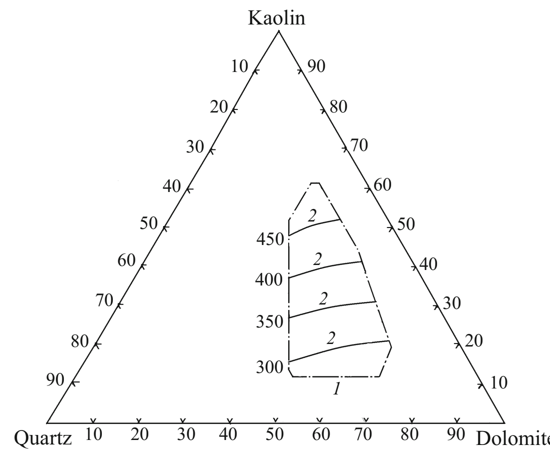

Fig. 6. Heat resistance of the synthesized glasses: *1*) boundary of the experimental glasses; *2*) heat resistance of the glasses.

Al_2O_3 content in the glasses raises the softening onset temperature.

The softening temperature fluctuates from 800 to 950°C depending on the chemical composition. It was determined that the softening onset temperature increases with increasing content of SiO_2 and partially Al_2O_3 in the experimental glasses and decreases with increasing amount of CaO and MgO, i.e., it depends directly on the strength of the bonds between the ions. As SiO_2 content increases, the degree of polymerization of the structural framework of $[SiO_4^-]$ tetrahedra increases, which causes temperature to have a loosening effect.

The dependence of the heat resistance of the glasses on their composition is presented in Fig. 6.

Analysis of the composition dependences of the properties of the glasses showed that the isolines do not have a kink but rather they are smooth functions of the composition.

The comparatively low CLTE and high softening temperatures attest to the high strength of the bonds in the experimental glasses. This suggests that their chemical stability is high. As the experimental data have shown, the glasses are highly resistant to water and alkali solutions and exhibit a quite high resistance to acids — the mass losses were 0.15 – 1.65% in 35% NaOH and 0.90 – 2.25% in 1 N HCl.

In summary, alkali-free glasses distinguished by low CLTE and high heat resistance have been obtained. They possess a high softening temperature and chemical resistance to water and alkali solutions. The synthesized glasses can be used to obtain glass crystalline materials for technical purposes.

Determining the composition dependence of the properties of the glasses in the system kaolin – quartz – dolomite made it possible to select the glass compositions to be used as the initial compositions when planning the compositions of sitals with prescribed and regulatable properties.